

# The Hartree - Fock method

given a Hamiltonian  $H$

$\Rightarrow$  approximate many-body ground state  
by single Slater determinant

$\rightarrow$  A occupied single-particle states  $|i\rangle$   
yield many-body state

$$|\phi\rangle = a_{i_1}^+ \dots a_{i_A}^+ |0\rangle$$

$\rightarrow |\phi\rangle$  has occupation numbers  $n_i$   
and energy  $\langle\phi|H|\phi\rangle = \sum_i n_i H_{ii}^{(1B)} + \frac{1}{2} \sum_{ij} n_i n_j H_{ij}^{(2B)}$

$\rightarrow$  Optimize states  $|i\rangle \rightarrow |\tilde{i}\rangle \Rightarrow |\tilde{\phi}\rangle$   
to yield minimal energy

This lecture:

- 1) Hartree-Fock in coordinate space
- 2) HF algorithm

## HF in coordinate space

- our Hamiltonian is

$$H = T + V_{NN} + V_{3N}$$

- true ground state  $|4\rangle$  has minimal energy:

$$E_{gs}^{\text{exact}} = \frac{\langle 4 | H | 4 \rangle}{\langle 4 | 4 \rangle}$$

$$\delta E_{gs}^{\text{exact}} = 0 \text{ for } \delta |4\rangle \text{ or } \delta \langle 4 |$$

- HF: seek Slater det. with minimal energy

$$\rightarrow |i\rangle_{HP} \text{ with orbitals } \phi_i(\vec{r}) = \langle \vec{r} | i \rangle_{HF}$$

$$\rightarrow |\phi\rangle_{HF} = a_1^+ \dots a_A^+ |0\rangle$$

$$\rightarrow E_{gs}^{HF} = \frac{\langle \phi_{HF} | H | \phi_{HF} \rangle}{\langle \phi_{HF} | \phi_{HF} \rangle} \geq E_{gs}^{\text{exact}}$$

$\Rightarrow$  best approx. of  $E_{gs}$  in space of single Slater determinant

Q: Is this ever exact (not an approximation)?

- Seek to optimize orbitals  $\phi_i(\vec{r})$   $i=1, \dots, A$   
 $\Rightarrow \delta E_{gs}^{\text{HF}} = 0$  for  $\delta\phi_i(\vec{r})$  or  $\delta\phi_i^*(\vec{r})$

HF at a high level

Input:  $V_{NN}$ ,  $V_{3N}$

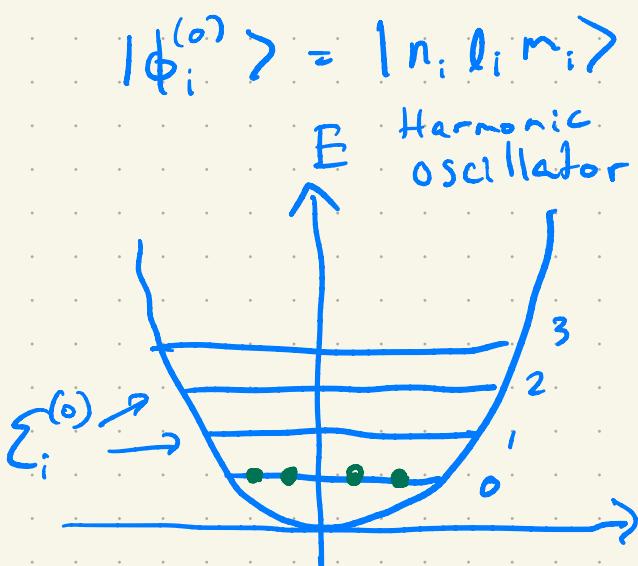
Solve: HF equations  $\leftarrow$  coupled Schrödinger-like equations

Obtain: optimized  $\phi_i^{\text{HF}}(\vec{r})$ ,  $E_{gs}^{\text{HF}}$ ,  $\varepsilon_i$ .

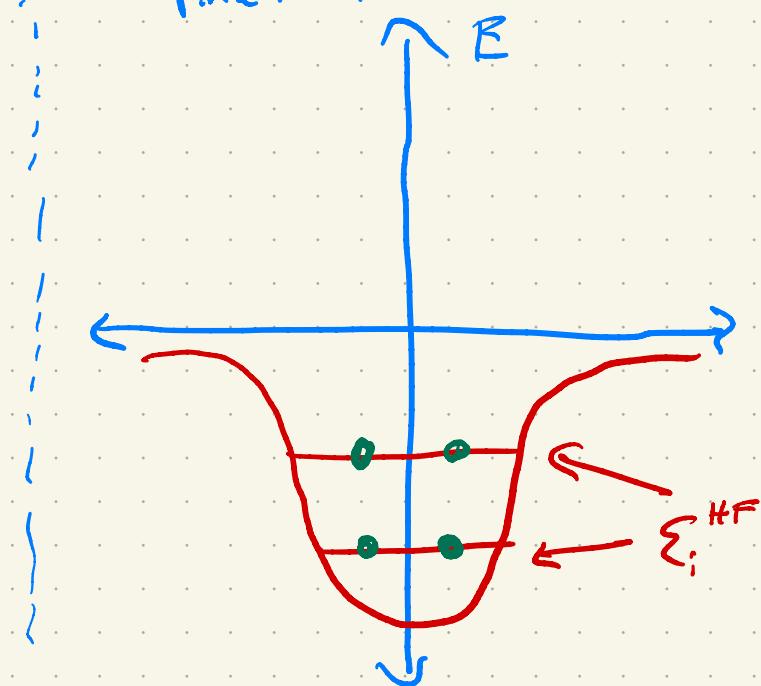
↑  
single-particle energies  
What are these?

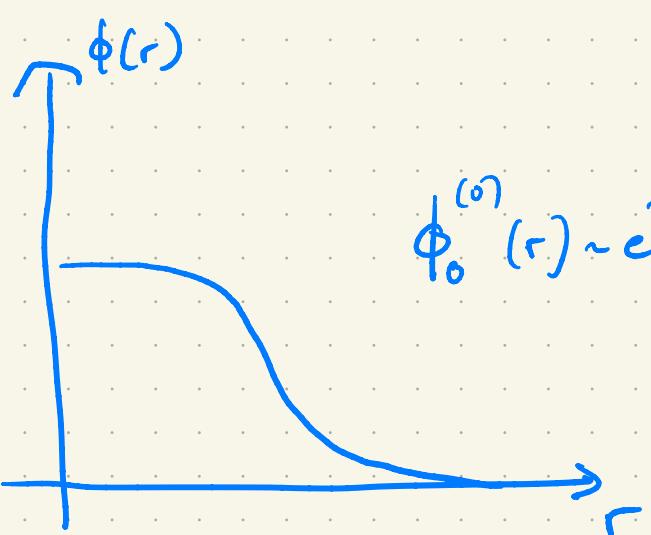
Example: for finite nuclei

starting point is HO basis:

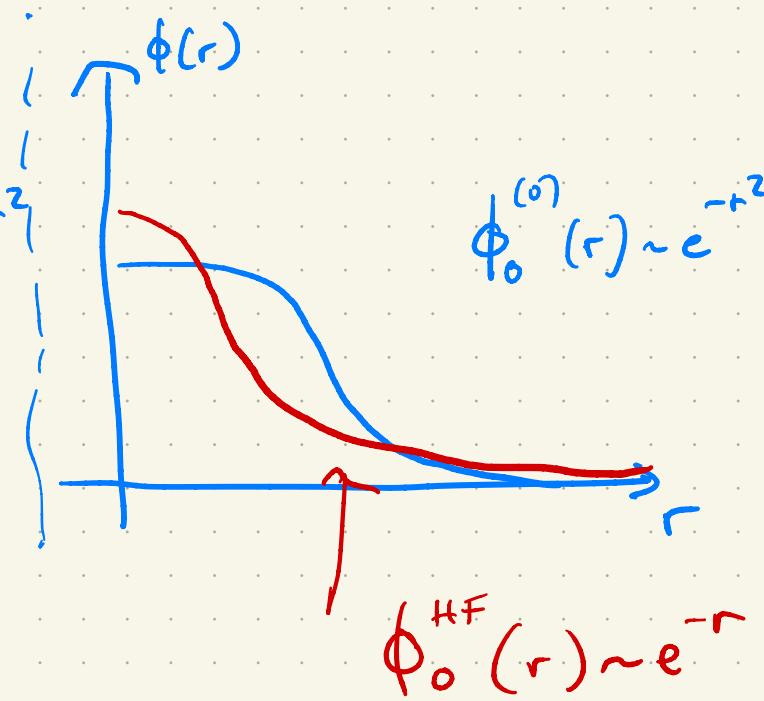


final HF basis





$$\phi_0^{(0)}(r) \sim e^{-r^2}$$



⇒ HF computes the average potential  
felt by nucleons to optimize orbitals  
→ "mean-field"

# HF in coordinate space (no derivation just main results)

(consider local potential)

$$H = \sum_{i=1}^A \frac{\vec{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j=1}^A V(|\vec{r}_i - \vec{r}_j|)$$

$$\langle \phi_{HF} | H | \phi_{HF} \rangle$$

$$= \sum_{i=1}^A \int d^3 r_i \phi_i^*(\vec{r}) \left( -\frac{1}{2m} \vec{\nabla}_i^2 \right) \phi_i(\vec{r})$$

$$+ \frac{1}{2} \sum_{i \neq j=1}^A \int d^3 r_i \int d^3 r_j \times$$

$$\left[ \phi_i^*(\vec{r}) \phi_j^*(\vec{r}') V(|\vec{r} - \vec{r}'|) \phi_i(\vec{r}) \phi_j(\vec{r}') \right]$$

$$- \phi_i^*(\vec{r}) \phi_j^*(\vec{r}') V(|\vec{r} - \vec{r}'|) \phi_j(\vec{r}) \phi_i(\vec{r}')$$

direct term  $\rightarrow$

exchange term  $\rightarrow$

to derive consider variation of  $\phi_i$  and demand that it is stationary

$$\delta (\langle \phi_{HF} | H | \phi_{HF} \rangle) \stackrel{!}{=} 0$$

Q: Is this enough?  $\Rightarrow$  No

$\phi$ : must also stay normalized

→ variation under constraint

⇒ Lagrange multipliers  $\Sigma_i$ :

Complete stationary condition:

$$\delta \left( \langle \phi_{HF} | H | \phi_{HF} \rangle - \sum_{i=1}^A \Sigma_i \int d^3r \phi_i^*(\vec{r}) \phi_i(\vec{r}) \right) = 0$$

Result:

from direct term

1) 
$$-\frac{1}{2m} \vec{\nabla}_{\vec{r}}^2 \phi_i(\vec{r}) + \left[ \int d^3r' V(|\vec{r}-\vec{r}'|) \sum_{j=1}^A \phi_j^*(\vec{r}') \phi_j(\vec{r}') \right] \phi_i(\vec{r}) = V_H[P](\vec{r})$$

=  $P(\vec{r}, \vec{r}')$  diagonal density matrix

from exchange + term

2) 
$$- \left[ \int d^3r' V(|\vec{r}-\vec{r}'|) \sum_{j=1}^A \phi_j^*(\vec{r}') \phi_j(\vec{r}) \phi_i(\vec{r}') \right]$$
  
 $V_F[P](\vec{r}, \vec{r}')$   $P(\vec{r}, \vec{r}')$   $f_{nn}$  density matrix

$$= \Sigma_i \phi_i(\vec{r})$$

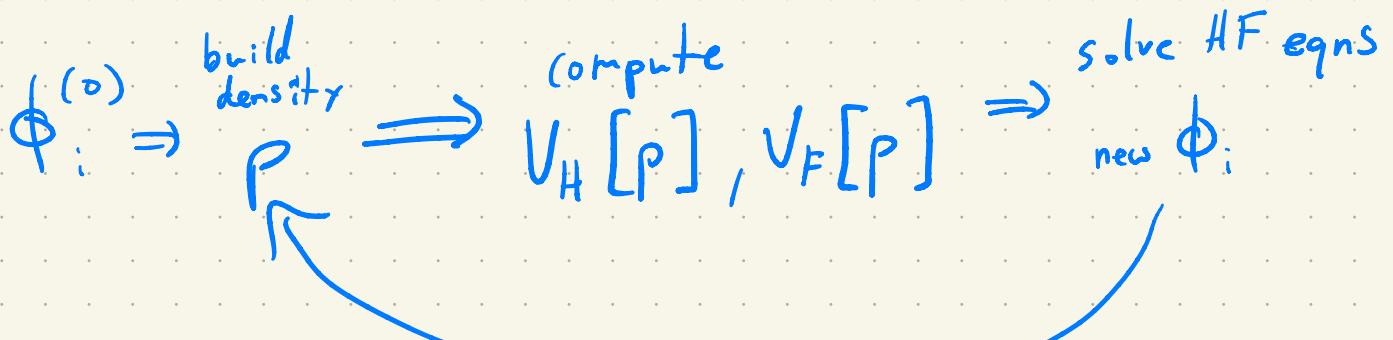
$$1) \text{ Hartree term} = V_H[\rho](\vec{r}) \phi_i(\vec{r})$$

- local:  $V_H$  dep. only on  $\vec{r}$ , not  $\vec{r}'$   
(after integral)
- dep. on diag density matrix
- easy to compute
- comes from direct term

$$2) \text{ Fock term} = \int d^3 r' V_F[\rho](\vec{r}, \vec{r}') \phi_j(\vec{r}')$$

- nonlocal potential  $V_F$  dep. on  $\vec{r}, \vec{r}'$
- dep. on full density matrix
- hard to compute
- comes from exchange term

HF equations solved by iteration



→ until iterative scheme converges

# HF algorithm

Input:  $V_{pqrs}^{(2B)}$ ,  $V_{pqrs tu}^{(3B)}$ ,  $T_{pq}^{(1B)}$

all in starting basis  $|P\rangle$

Approach:

→ new basis  $|\bar{P}\rangle$  from starting basis  $|P\rangle$

$$\rightarrow |\bar{P}\rangle = \sum_P |P\rangle \langle P| \bar{P}\rangle$$

$$= \sum_P C_{\bar{P}P} |P\rangle$$

↑

expansion coeffs

→ iteratively optimize  $|\bar{P}\rangle$

⇒ get better Slater det.

$$|\bar{\phi}\rangle = b_{\bar{P}_1}^+ \dots b_{\bar{P}_A}^+ |0\rangle$$

⇒ equivalently get better one-body density matrix

$$P \leftrightarrow |\bar{\phi}\rangle$$

$$|\rho\rangle \Rightarrow \rho \Rightarrow F \Rightarrow |\bar{\rho}\rangle$$

↑  
Fock matrix

⇒

Need to know:

- 1) how to compute one-body density matrix  $\rho$  from basis  $|\bar{\rho}\rangle$
- 2) how to compute Fock matrix  $F$  from density  $\rho$  and Hamiltonian
- 3) diagonalize Fock matrix  $F$  to get new basis  $|\bar{\rho}\rangle$  and associated single-particle energies

$$\epsilon_{\bar{\rho}}$$

Before we start:

→ need to identify occupation numbers  $n_{\bar{p}}$

for HF state  $|\bar{\phi}\rangle = |\bar{p}_1 \bar{p}_2 \dots \bar{p}_A\rangle$

$$n_{\bar{p}} = \begin{cases} 1 & \text{if } \bar{p} \in \{\bar{p}_1, \dots, \bar{p}_A\} \\ 0 & \text{otherwise} \end{cases}$$

Q: How do we know the right occupation numbers?

Not always perfect, but take  $|\bar{p}\rangle = |p\rangle$  and fill lowest A states

i) Computing density matrix

→ need  $n_{\bar{p}}$ ,  $C_{\bar{p}\bar{p}}$

$$\rightarrow P_{Pq} = \sum_{\bar{p}\bar{q}} C_{\bar{p}\bar{p}} n_{\bar{p}} \delta_{\bar{p}\bar{q}} C_{\bar{q}\bar{q}}^*$$

one-body  
matrix elements

$$= \sum_{\bar{p}} (C^T)_{\bar{p}\bar{p}} n_{\bar{p}} C_{\bar{p}\bar{q}}^*$$

$\rightarrow P_{pq}$  is a representation of  $|\bar{\phi}\rangle$  in starting basis  $|p\rangle$

Remark: one-body density matrix is more general representation of Slater determinant  $|\bar{\phi}\rangle$  than occupation number  $n_{\bar{p}}$ .

$\rightarrow$  works in arbitrary basis

$\rightarrow P_{\bar{p}\bar{q}} = n_{\bar{p}} \delta_{\bar{p}\bar{q}}$  in HF basis  $|\bar{p}\rangle$

## 2) Computing Fock matrix

$\rightarrow$  need  $P_{pq}$ ,  $H_{pq}^{(1B)}$ ,  $H_{pqrs}^{(2B)}$   
 kinetic energy,  
 external potential      two-body interactions

[if required  $H_{pqrsstu}^{(3B)}$ ]

$$F_{pq} = H_{pq}^{(1B)} + \sum_{rs} p_{rs} H_{pqrs}^{(2B)}$$

↑  
pay attention to order

Aside: energy associated with  $P$   
easily computed

$$E = \sum_{pq} P_{pq} H_{pq}^{(1B)} + \frac{1}{2} \sum_{\substack{pq \\ rs}} P_{pq} P_{rs} H_{pqrs}^{(2B)}$$

→ Check that  $E$  decreases each time  
you get an updated density matrix  
 $P$

3) diagonalizing Fock matrix

→ input:  $F$

new basis  $| \bar{p} \rangle$  solves

$$F | \bar{p} \rangle = \varepsilon_{\bar{p}} | \bar{p} \rangle$$

⇒  $|\bar{p}\rangle$  is eigenbasis of  $F$

⇒ eigenvalues are single-particle energies

→ output: new  $C_{\bar{p}p}$

Overall approach:

→ solve iteratively:

$$C_{\bar{P}P}^{(i)}, P^{(i)}, F^{(i)}, E_{gs}^{(i)} \rightarrow C_{\bar{P}P}^{(i+1)}$$

→ convergence reached if

$$\left| E_{gs}^{(i+1)} - E_{gs}^{(i)} \right| < \epsilon_{conv}$$

reasonable choice:  $\epsilon_{conv} = 10^{-4}$

Exercises today:

- solve HF for simple Hamiltonian
- get used to matrix elems, basic equations

⇒ Tomorrow: HF for nuclei

→ same method

→ more complicated Hamiltonian

→ bigger basis